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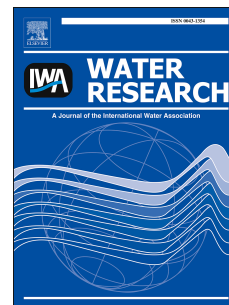
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# Accepted Manuscript

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## Acidification and recovery of phosphorus from digested and non-digested sludge

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### Abstract

Acidification was used to dissolve phosphorus from digested and non-digested sludge from five wastewater treatment plants in order to make phosphorus accessible for subsequent recovery. More phosphorus was dissolved from digested sludge (up to 80%), with respect to non-digested sludge (~25%) and the highest recovery was observed at pH 2. The acid consumption for digested sludge was higher than for non-digested sludge due to the presence of the bicarbonate buffer system, thus CO<sub>2</sub> stripping increased the acid consumption. In all the experiments, the sludge was exposed to acid for 1h. For the five tested sludge types, 60-100 mmol o-P was released per added mol H<sub>2</sub>SO<sub>4</sub>. It was mainly iron and calcium compounds that accounts for the phosphorus release at low pH. The release of heavy metals was in general low (<30%) for all the wastewater treatment plant, as Zn, Cd and Ni showed the most critical release after acidification of non-digested sludge.

**Keywords:** *Phosphorus, acidification, sludge, heavy metals*

### Introduction

The human population will grow to 9.3 billion by 2050, meaning that food production needs to increase accordingly. A high production of agricultural products can only be achieved by the use of fertilizers of

which nitrogen, phosphorus and potassium are usually deficient in the soil. The P-fertilizers used today almost exclusively comes from mining of phosphate rocks, which are estimated to be depleted by the end of this century (Cordell et al., 2009; Shu et al., 2006). Consequently, it is necessary to recycle phosphorus to ensure food security for future generations. Recovery of phosphorus from wastewater is one method to overcome the possible phosphorus scarcity. Wastewater contains large amounts of phosphorus and the Danish Environmental Protection Agency has estimated that it eventually can cover around 20% of the total phosphorus import in Denmark (Miljøministeriet (The Danish Environmental Protection Agency), 2013). Moreover, Denmark is exporting agricultural products (mainly meat and dairy products), thus phosphorus is also leaving the country (Klinglmair et al., 2015). In Denmark, the ratio of out- to inflows of phosphorus is 0.66, which is higher compared to the EU (0.27) (Klinglmair et al., 2015). In 2013, the Danish government had an ambition to increase the phosphorus recycling from sewage sludge from 50-55% to 80% (The Danish Government, 2013). Therefore, new and improved methods for phosphorus recycling and recovery needs to be developed. In this study, we explore the potential to improve phosphorus recovery by sludge acidification of various sludge types from different wastewater treatment plants in Denmark. Today, phosphorus in wastewater is usually removed biologically or chemically to meet discharge criteria whereby the phosphorus ends up in sewage sludge. Sewage sludge can be used directly as a fertilizer, but in several countries in Europe (Tarayre et al., 2016), land spreading of sludge is banned as sludge may be contaminated by heavy metals, pathogens and toxic organic compounds (Vardanyan et al., 2018). If sludge is incinerated, phosphorus can be recovered from the ash, but it is still an expensive method and it has been questioned, whether incineration and recovery of phosphorus from ash is a sustainable technology (Vaneckhaute et al., 2017). An alternative method is to recover and recycle dissolved phosphorus through precipitation from the liquid phase after removal of the solid material. For instance, phosphorus can be precipitated from the centrate or filtrate after dewatering of digested sludge. Some wastewater treatment plants has implemented fluidized bed reactors to recover phosphorus from liquid phase by adding magnesium and precipitating struvite ( $\text{MgNH}_4\text{PO}_4 \cdot 7\text{H}_2\text{O}$ ) (Cordell et al., 2011). However, Hermann et al. (Hermann, 2009) and Pinnekamp et al. (Pinnekamp et al., 2013) states that only 30-50 % of all the phosphorus present in the wastewater can be recovered by this technique depending on the efficiency of the biological phosphorus

removal process. A large fraction of phosphorus in sludge exists as particulate phosphorus including metal-salts e.g. calcium phosphates and iron phosphates, and phosphorus accumulated in microorganisms (as polyphosphate and in the cell wall) (Venkiteshwaran et al., 2018). Polyphosphate-accumulating organisms are embedded in the sludge flocs and removed with solid fraction during dewatering (Larsen et al., 2006). A part of the phosphorus stored in phosphate accumulation organism is released during digestion (Hu et al., 2018). Metals salts are also expected to end up in the solid phase (Meulepas et al., 2015). Thus, most of the phosphorus in the metal-salts and the microbial mass is expected to end up in the sludge and not in the liquid phase and the phosphorus content in the sludge is thus not accessible for phosphate recovery.

The current study focusses on phosphorus recovery through acidification, separation and phosphorus precipitation. Recent studies have shown that acidification of sludge increases the dissolved phosphorus concentration due to dissolution of the metal-phosphate-complexes (Latif et al., 2015). Low pH anaerobic digestion can be utilized, but it reduces the biogas production (Latif et al., 2015). Alternatively, sludge can be acidified after digestion, which has previously been done by Antakyali et al. (Antakyali et al., 2013), Shiba and Ntuli (Shiba and Ntuli, 2017) and SEG et al. (SEG - Stadtentwässerung Göppingen et al., 2014), who acidified digested sewage sludge and precipitated struvite on a large-scale plant (The Stuttgart Process). The results showed a dissolution of phosphorus by 75%, which enhances the recovery of the subsequent struvite precipitation process to around 98%. The purity of the product has not been reported (Antakyali et al., 2013). One of the potential negative consequence of acidification, is the simultaneously dissolution of iron, aluminium, and heavy metals (Wozniak and Huang, 1982). The purity of the phosphorus product might decrease and thereby lowering the value of the phosphorus product as a fertilizer. However, the requirements of purity depends on if the phosphorus product is used directly or as a raw material for producing fertilizers. To avoid precipitation of iron phosphate, citric acid has been added to bind iron, which increase the costs of the process (SEG - Stadtentwässerung Göppingen et al., 2014). Alternatively, iron can be removed by ion exchange (Shiba and Ntuli, 2017). In the Gifhorn process, sulfuric acid and  $\text{Na}_2\text{S}$  is used for acidification to dissolve phosphorus and remove interfering ions such as iron by sulfidic precipitation (Amann et al., 2018;

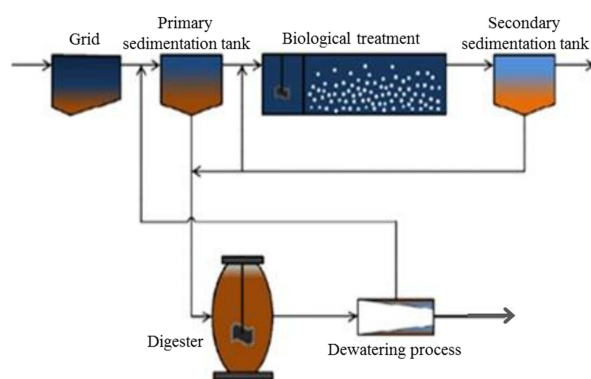
Tarayre et al., 2016). Phosphorus is then precipitated as a mixture of struvite and calcium phosphate at pH 9 (Tarayre et al., 2016). In the Seaborn Process hydrogen sulfide from the digester tank is used to precipitate aluminium, iron and heavy metals (Müller et al., 2007). In the Budenheim process, sludge is aerated with CO<sub>2</sub> at 10 bars pressure to lower pH and dissolve phosphorus (Stössel, 2013). Phosphorus precipitate as calcium phosphate and most of the CO<sub>2</sub> is recycled during the process (Stössel, 2013). (Levlin and Hultman, 2007) suggested a two-step process. In the first step, acetic acid is added to reduce pH to 4, whereby part of the phosphorus is dissolved and ends up in the liquid after solid-liquid separation; iron- and aluminium phosphate is not dissolved and ends up in the solid materials. In the second step sodium hydroxide is added to the solid material from the first step, whereby phosphorus from iron- and aluminium phosphate is dissolved. Iron and aluminium is precipitated as iron- and aluminium hydroxide and removed with the solid material. Phosphorus is then precipitated as struvite and calcium phosphate (Levlin and Hultman, 2007). Thus, if sludge cannot be used directly as a fertilizer; three commercial alternatives exist: recovery from the liquid phase, recovery from the sludge and recovery from the ash. These methods vary in the amount of phosphorus that can be recovered and the need of chemicals that have to be added (Amann et al., 2018).

In this study, we explore the potential to improve phosphorus recovery by means of sludge acidification. Sludge from five different wastewater treatment plants in Denmark has been used - both digested (primary and secondary sludge) and non-digested sludge (secondary sludge) has been used. The aim is to maximize the phosphorus release after acidification and to study the rate of iron, aluminium and heavy metal dissolution.

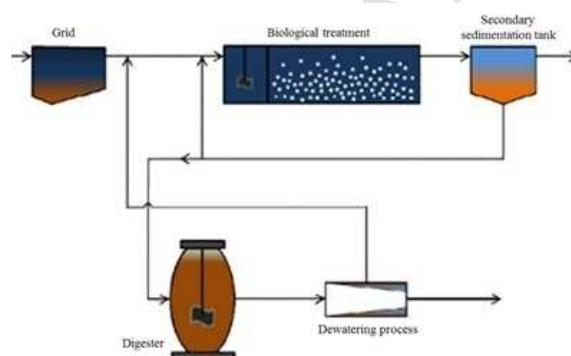
## Materials and methods

### *Description of the wastewater treatment plants*

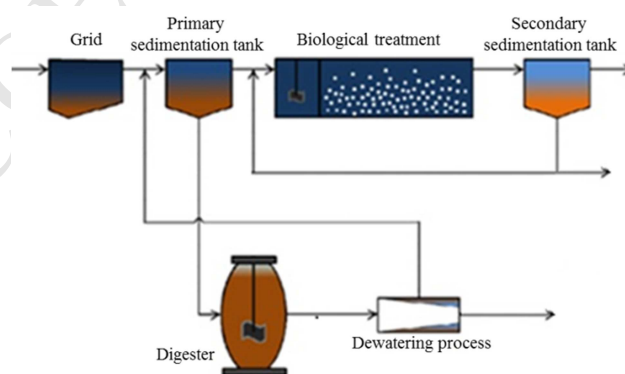
Wastewater sludge samples were collected from five wastewater treatment plants (WWTPs) located in different cities in Denmark i.e. Randers, Aaby, Skagen, Kolding and Haderslev. The WWTPs located in Randers and Skagen are characterized by digesting both primary and secondary sludge (Figure 1a), Aaby



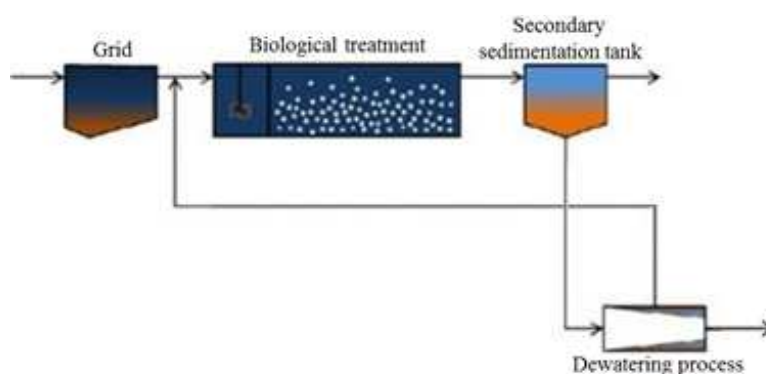
(a)



(b)



(c)



(d)

Figure 1: Flow sheet for the wastewater treatment plants, a) Randers and Skagen; b) Aaby; c) Kolding; d) Haderslev

Data for inlet flow and phosphorus concentration of the raw wastewater is shown in Table 1. The amount of phosphorus removed by the biological and chemical process varies between 80-95% for the different plants. These data are average values provide by the wastewater treatment plants and the details of the sludge analyzed in this study can be found in Table 2 and Table 3.

Table 1: Characteristics of the wastewater treatment plants.

	Sludge type	Inlet flow [m <sup>3</sup> /d] <sup>a</sup>	Inlet phosphorus concentration [mg/L] <sup>a</sup>	Outlet phosphorus concentration [mg/L] <sup>a</sup>
Randers WWTP	Digested (Primary + secondary)	23,150	6.78	0.42
Aaby	Digested (Secondary)	16,874	6.70	0.34
Skagen	Digested (Primary + secondary)	8,736	20	0.47
Kolding WWTP	Digested (Primary)	28,449	6.20	1.03
Haderslev WWTP	Non-digested (Primary + secondary)	10,953	7.75	0.45

<sup>a</sup> Average values provided by the wastewater treatment plants



### Acidification of sludge

Sludge samples from each WWTP were collected after digestion but prior to dewatering except for Haderslev where excess sludge from the secondary treatment process was collected. A series of experiments were performed where 100 ml of sludge was acidified by 0.5 M H<sub>2</sub>SO<sub>4</sub> to pH 4, 5, 6, 7 and 2 M H<sub>2</sub>SO<sub>4</sub> to pH 2 and 3. The 2M H<sub>2</sub>SO<sub>4</sub> solution was used at the lower pH in order to reduce dilution of the sludge samples. In addition, 100 ml of sludge was collected and pH increased to pH 11 by adding 2 M NaOH. All sludge samples (with sulfuric acid, sodium hydroxide or no treatment) was centrifuged at 2880 G for 3 minutes and filtered through a 0.45 µm filter. The concentration of ortho-phosphate (o-P), total phosphorus, metals and heavy metals were measured. One series of experiments (one for each type of sludge) were carried out in order to test the rate of phosphorus dissolution by reducing pH to 2.5, after which o-P was analyzed after 10 min and up to 5 h. The concentration of o-P was almost constant during the whole time period; thus for all samples reported in this paper, the samples were left for stirring for 1 h after addition of sulfuric acid or sodium hydroxide.

The o-P concentration was measured in the filtrate, whereas the total phosphorus concentration was measured before centrifugation and filtration. Both ortho-phosphate and total-phosphorus was measured as described in the Danish Standards (Danish Standard, 1985a, 1985b). The o-P release was estimated according to equation 1:

$$\text{o-P release [\%]} = \frac{[\text{o-P}]}{[\text{t-P}]} \cdot 100 \quad (\text{eq. 1})$$

where [o-P] is the concentration of o-P in the filtrate after sludge acidification and [t-P] is the concentration of total phosphorus in the sludge.

Concentration of metals and heavy metals was analyzed in the filtrate by inductively coupled plasma optical emission spectrometry (ICP-OES) and compared to the concentration of metals in the sludge before acidification. The ICP-OES was a Thermo Scientific iCap 6300 operated in axial view mode. The spectrometer was calibrated against matrix matched multi element standards. The dry matter content of the

149 samples was estimated by leaving around 15 g of raw sludge in a drying oven at 105 °C for 24 hours.  
 150 Afterwards, the dry matter was incinerated at 550 °C for 2 h to determine the organic/inorganic matter. The  
 151 weight loss was determined as the organic matter, whereas the inorganic part was determined as from the  
 152 weight that remains incineration at 550 °C.

### 153 *Sludge analysis*

154 Potentiometric titrations were performed using Titralab™ 900 equipment from Radiometer Denmark, and a  
 155 SI Analytics Blue Line 17 pH glass electrode calibrated against standard buffer solution at pH 4 and 7.  
 156 Diluted samples were prepared dissolving 1 mL sludge samples in 19 mL 0.1 M NaClO<sub>4</sub>. All experiments  
 157 were performed at 23 °C under a nitrogen atmosphere by stepwise adding 100 mM H<sub>2</sub>SO<sub>4</sub> until pH reached  
 158 pH3, then the experiment was stopped. The buffer capacity was calculated according to eq. 2.

$$159 \quad \beta = \frac{dn}{dpH} \quad (\text{eq. 2})$$

160 where,  $\beta$  is the buffer capacity,  $dn$  denotes the changes of moles acid added to the sludge and  $dpH$  denotes  
 161 the equal changes in pH. It is assumed that the acid is completely dissociated. The second dissociation  
 162 constant for sulfuric acid is  $1.2 \cdot 10^{-2}$  M; thus at pH 3 less than 10% of the sulfuric acid is present as HSO<sub>4</sub><sup>-</sup>.  
 163 The alkalinity is equal to the amount of strong acid required to lower pH to 4.5 and can be calculated by  
 164 integrating the buffer capacity from pH 4.5 to the initial pH value. The alkalinity is often used as a measure  
 165 of the bicarbonate/carbonate concentration, but a more precise analysis is possible by plotting the buffer  
 166 capacity as function of pH.

167 Particle size distributions were analyzed using a laser diffraction particle size analyzer (Beckman & Coulter  
 168 LS 13320) with universal liquid module. The Fraunhofer theory was used for data treatment, and tap water  
 169 was used for background measurements. The experiments were replicated twice. Sludge before and after  
 170 acidification has been analyzed by light microscope (Zeiss Axioskop) connected to a computer in order to  
 171 identify the floc structure. The sludge has been spread on a glass plate and imaging through the microscope.

### 172 *Separation and precipitation of phosphorus*

Sludge samples from Randers and Kolding were acidified to pH 2. The solid material was removed by centrifugation at 2800 G for 3 minutes and the supernatant was filtered through a 0.45  $\mu$ m filter. Phosphorus was precipitated from the liquid phase by adding 2M NaOH to pH 6, 7, 8, and 9, respectively. The precipitate was removed by centrifugation, weighed and analyzed by ICP-OES.

## Results and discussion

### *Raw sludge analysis*

Sludge from five different WWTPs was collected and analyzed (Table 2). At the WWTPs with a digester, sludge is thickened before digestion; hence the digested sludge has a higher dry matter content than undigested sludge (Haderslev WWTP). Kolding WWTP, which only digests primary sludge, was found to have a slightly lower dry matter content than Randers, Aaby and Skagen WWTPs, where both primary and secondary sludge is digested. The highest fraction of organic matter was observed in the un-digested sludge from Haderslev as expected.

Table 2: Dry matter, organic and inorganic matter for the different sludge types

	pH	Dry matter [g/kg]	Organic matter [g/kg]	Inorganic matter [g/kg]
Randers WWTP	7.35	39.3	22.0 (56%)	17.3 (44%)
Aaby WWTP	7.1	42.1	28.4 (68%)	14.7 (32%)
Skagen WWTP	8.24	41.2	26.2 (64%)	15.0 (36%)
Kolding WWTP	7.31	31.4	19.1 (61%)	12.3 (39%)
Haderslev WWTP	6.60	15.4	11.1 (72%)	4.23 (28%)

The composition of sludge has been analyzed (Table 3). All concentrations were lower in the non-digested sludge as the dry matter content of the sludge was low. The concentration of iron varied between the different plants depending on the wastewater treatment process and how much iron that was added to reduce the amount of discharged phosphorus. The concentration of iron in Aaby WWTP was relatively low as

phosphorus was removed biologically in the secondary treatment process. The concentration of iron was also low in Kolding WWTP, as no iron is added during the primary wastewater treatment (Table 1). The concentrations of heavy metals was high at Kolding WWTP. The reason for this is not known.

Table 3: Composition of the different sludge types.

	total-P mg/gTS	Ca mg/gTS	Mg mg/gTS	Al mg/gTS	Fe mg/gTS	Cd mg/gTS	Cr mg/gTS	Cu mg/gTS	Ni mg/gTS	Pb mg/gTS	Zn mg/gTS
Randers WWTP	33.1	39.0	5.78	8.2	45.9	0.00168	0.0298	0.187	0.0442	0.0657	1.17
Aaby WWTP	33.6	28.2	7.68	6.7	22.2	0.00111	0.0172	0.217	0.0302	0.0542	0.627
Skagen WWTP	32.1	14.8	4.19	3.2	72.6	0.00196	0.0110	0.0622	0.0219	0.0125	0.354
Kolding WWTP	37.6	51.1	3.90	14.1	16.3	0.00483	0.0641	0.457	2.30	0.114	2.92
Haderslev WWTP	23.5	25.4	5.61	5.9	30.4	0.000970	0.0626	0.140	0.0408	0.0446	0.798

The floc size has been measured (Table 4) and images are shown for all sludges (Figure 2). Activated sludge (Haderslev) had the largest floc structures (~80  $\mu\text{m}$ ). The floc size of digested sludge was slightly smaller than non-digested sludge and contained more fines and irregular flocs. The smallest floc size was observed in the digested primary sludge (Kolding). The floc structure was seemingly not fully broken down after acidification for all the sludge types but more fluffy flocs was obtained and more particles and filament was observed between the flocs (Figure 3).

Table 4: Size of sludge

	Mean [ $\mu\text{m}$ ]	Median [ $\mu\text{m}$ ]	S.D. [ $\mu\text{m}$ ]
Randers WWTP	130	73	160
Aaby WWTP	110	64	160
Skagen WWTP	90	63	110
Kolding WWTP	110	37	172
Haderslev WWTP	110	80	126

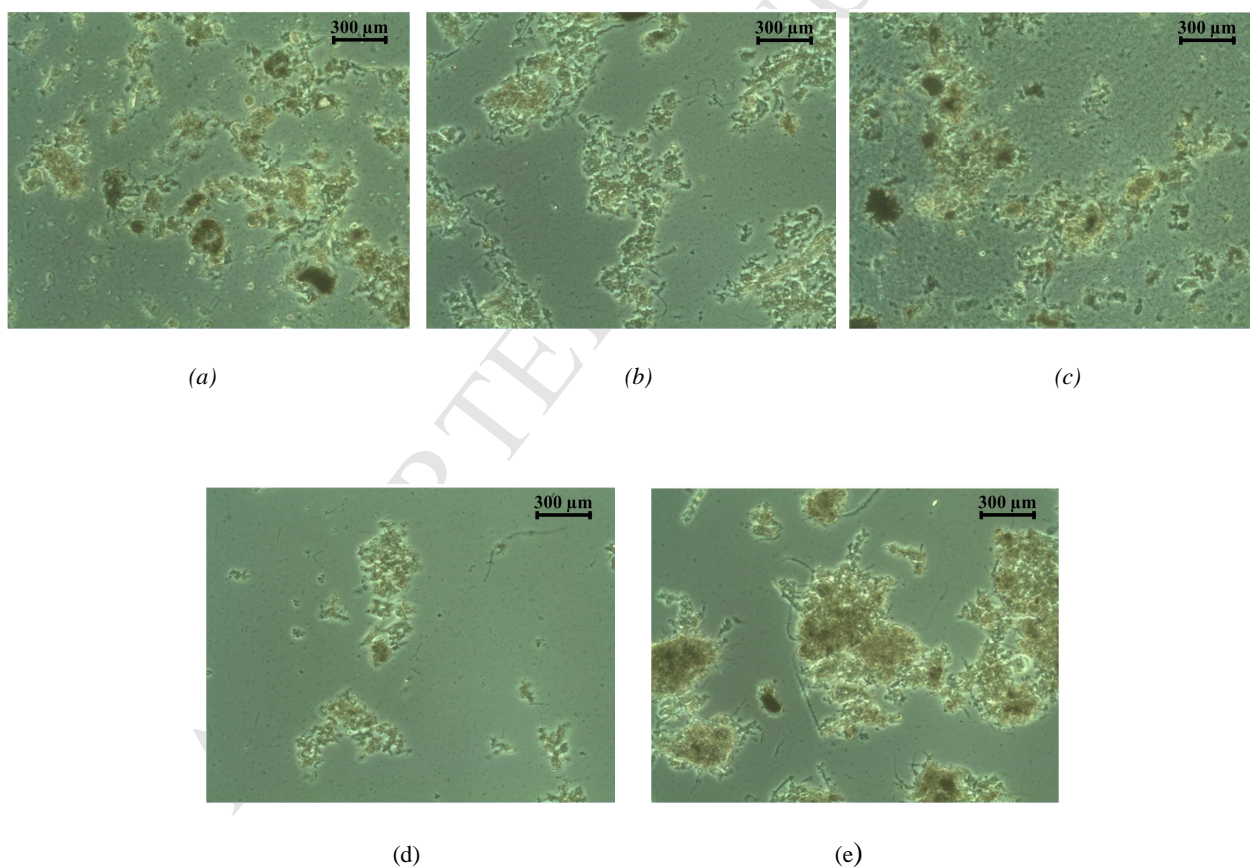


Figure 2: Floc structure in raw sludge (100x magnification) at (a) Randers; (b) Aaby; (c) Skagen; (d) Kolding; (e) Haderslev WWTP

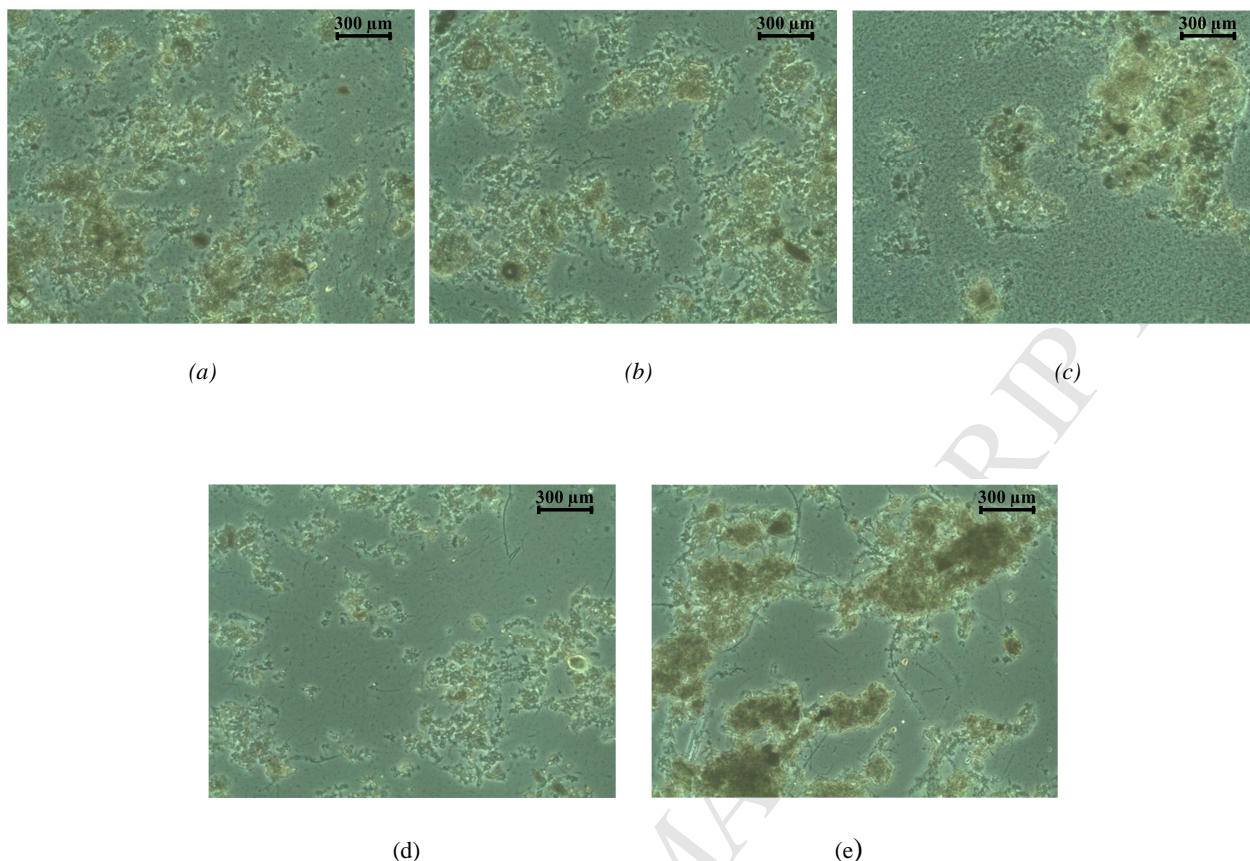


Figure 3: Floc structure at pH 3 (100x magnification) at (a) Randers; (b) Aaby; (c) Skagen; (d) Kolding; (e) Haderslev WWTP

### Sludge acidification

The sludge samples were acidified with sulfuric acid (Figure 4). The required amount of acid was lowest for the undigested sludge (Haderslev). In the digested sludge, more acid were consumed due to  $\text{CO}_2$  stripping as high amounts of carbonate were produced when the substrate were degraded to methane and carbonate (Chipasa, 2003). The removal of  $\text{CO}_2$  is illustrated by a buffer capacity plot (Figure 5), which corresponds well with the  $\text{H}_2\text{CO}_3/\text{HCO}_3^-$  equilibrium that has a  $\text{pK}_a$  value of 6.3.



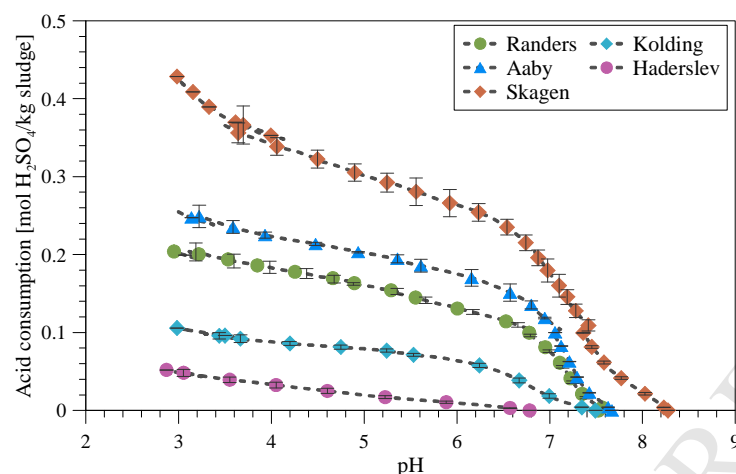


Figure 4: Acid consumptions for pH regulation of the different sludge types.

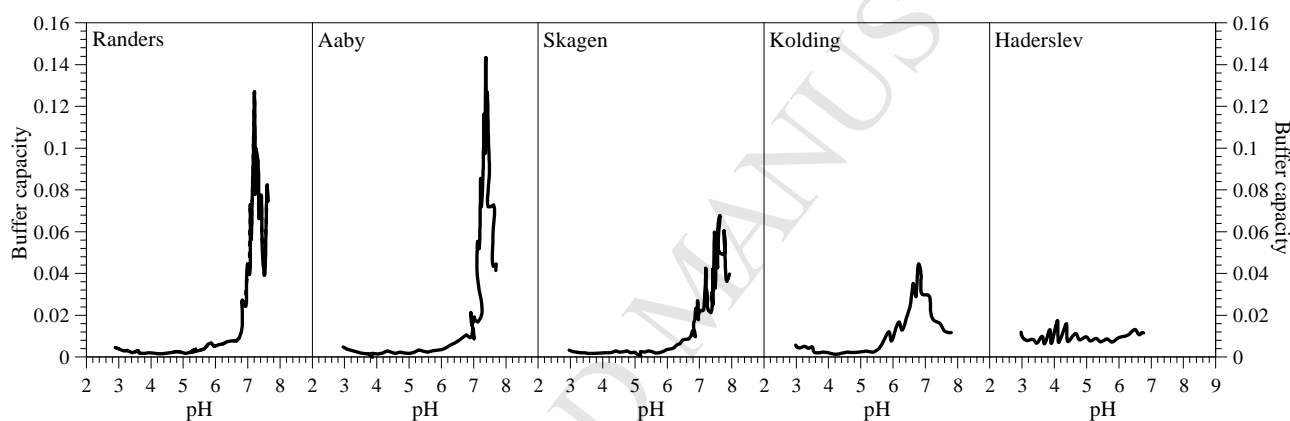


Figure 5: Buffer capacity for the different sludge types.

The released amount of dissolved ortho-phosphate (o-P) increased with decreasing pH (Figure 6) as observed in previous studies due to dissolving of mainly inorganic phosphorus (He et al., 2016; Xu et al., 2015). Digestion followed by acidification can release more than 80% of phosphorus, which corresponds with previous studies (Antakyali et al., 2013). Aaby WWTP has a higher amount of dissolved phosphorus at pH 7-8 (no acidification) compared to the other WWTPs. The Aaby plant is designed for biological P removal and has a fluidized bed reactor implemented to precipitate and extract struvite from the digester centrate. As already discussed, an optimized biological P removal during secondary treatment and P release during digestion can facilitate recovery of struvite or other P products, still the potential for phosphorus recovery

can be significantly improved by lowering pH to 3 prior to sludge dewatering. Contrary to the digested sludge, the non-digested sludge (Haderslev WWTP) shows low o-P release during acidification. Moreover, the inorganic matter (Table 2) from Haderslev WWTP is low, and thus the metal-phosphorus salt content also limits the o-P release. A slight increase in dissolved phosphorus is observed for sludge from Randers and Skagen when NaOH is added, but P release is low compared with the phosphorus release obtained by acidification. To conclude, acidification improve P removal - i.e. around 85% of the phosphorus was dissolved for WWTP handling mixed primary and secondary sludge that has been digested. For WWTPs using chemical P removal, acidification is the only feasible way to release and harvest phosphorus. Moreover, (Chen et al., 2001) found that acidification improves the dewaterability of activated sludge due to exocellular polymer (ECP) leaves the activated sludge surface, which makes it easier to pack the sludge and reduces the water content of the sludge. Therefore, acidification both increases phosphorus recovery and improve dewaterability. On the contrary, acidification limits the later use on agricultural land, but since land application is not allowed in many European countries and which is the reason for the acidification process (Tarayre et al., 2016), incineration is a more feasible method that at the same time produces energy (Lundin et al., 2004).

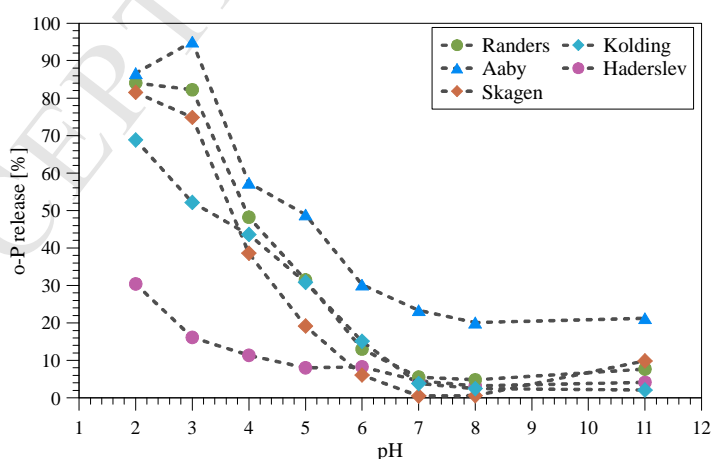


Figure 6: o-P concentration with respect to t-P concentration at different pH. Reaction time: 1h.

The required amount of acid for dissolving phosphorus is shown in Figure 7. The release of phosphorus increases almost linearly with the added amount of sulfuric acid. The regression line (dashed line) shows that



about 100 mmol o-P was released per added mol  $\text{H}_2\text{SO}_4$ , i.e. about 10 mole diprotic acid per mole o-P. The larger amount of acid used is due to  $\text{CO}_2$  stripping. It should be noticed that for Aaby WWTP, 10 mM o-P was dissolved when no acid was added. Still the extra release of phosphorus was the same as for the other sludge types e.g. 100 mmol o-P was released per added mol  $\text{H}_2\text{SO}_4$ . The lowest release of phosphorus as function of sulfuric acid dosage was observed for Skagen and Kolding. The phosphorus release was 25% lower for Skagen and 40% lower for Kolding.

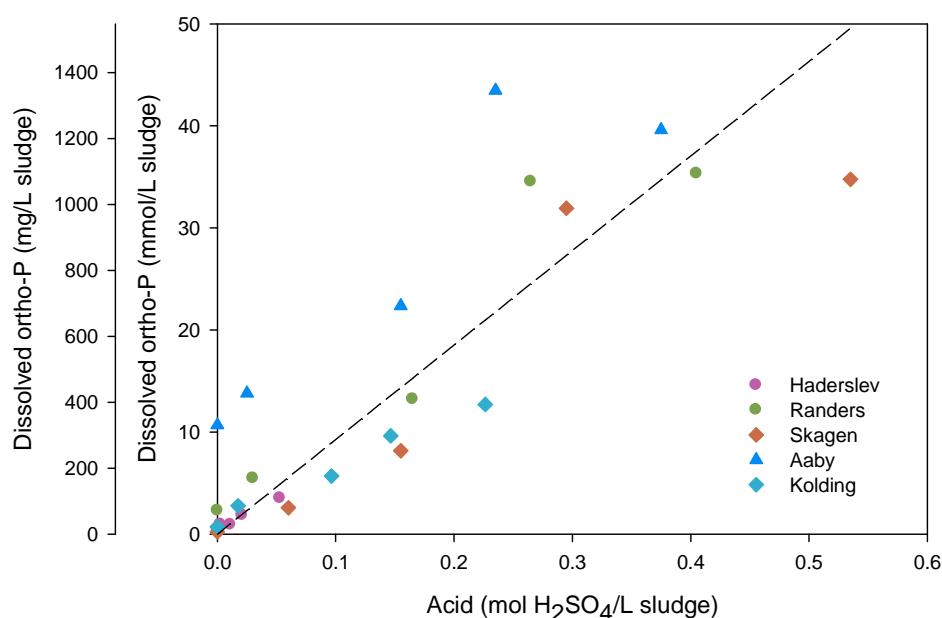


Figure 7: Acid consumption with respect to o-P release

#### *Dissolution of metals during acidification*

Most of the released phosphorus and carbonate originate from calcium, magnesium, aluminum and iron carbonates and phosphates. The metals in these compounds dissolve following the same trend as the phosphorus release at decreasing pH (Figure 8). Randers WWTP has a high total concentration of calcium and iron in the raw sludge and Kolding has a high concentration of calcium. The magnesium release is between 30% and 70% depending on the WWTP, but as magnesium is found in lower concentrations in the raw sludge (Table 3), it is not the main contributor to phosphorus release. Aluminum has in general a low

release and also a low concentration in raw sludge (Table 3), which is as expected as the WWTPs investigated are not adding aluminum during the wastewater treatment.

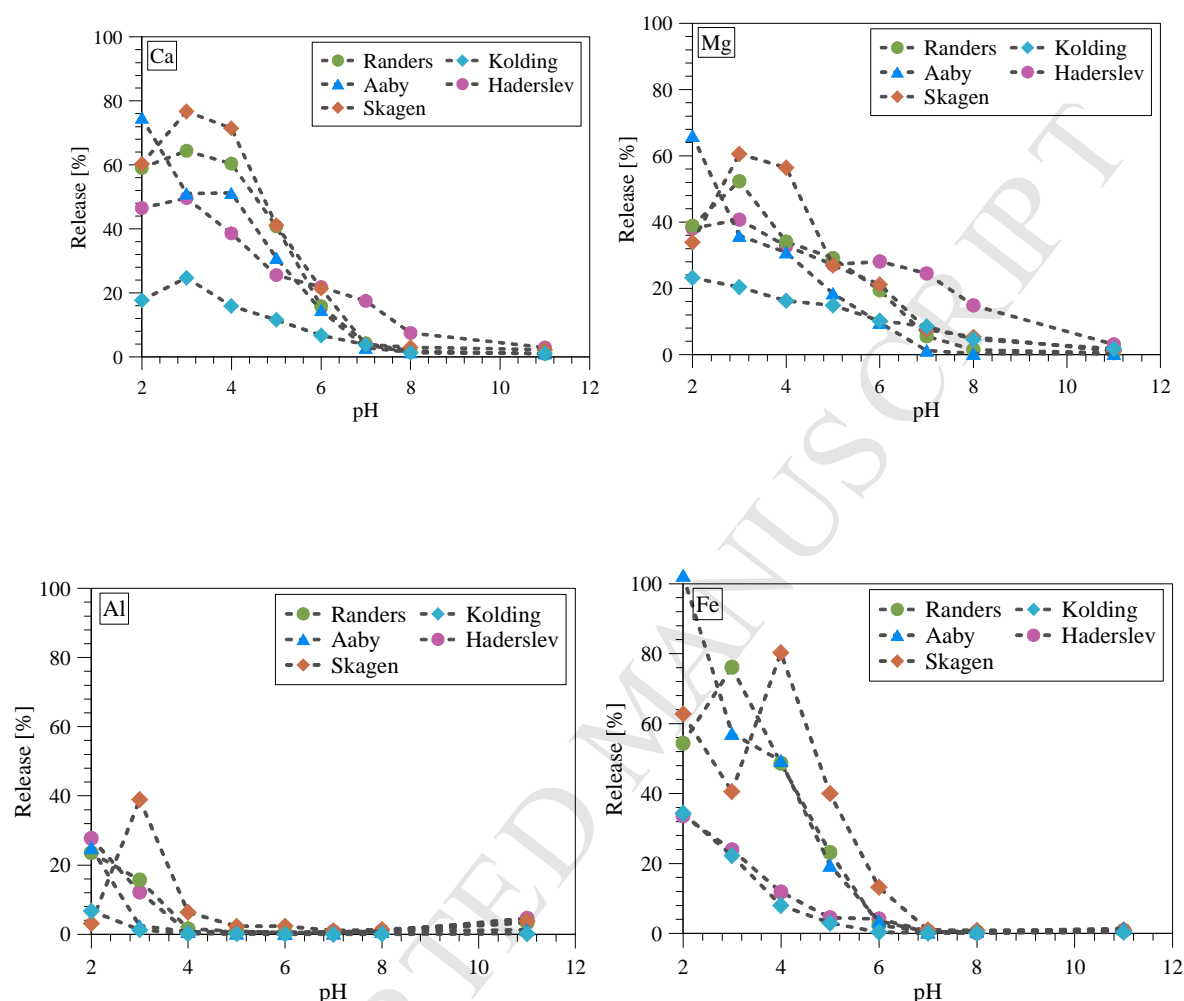
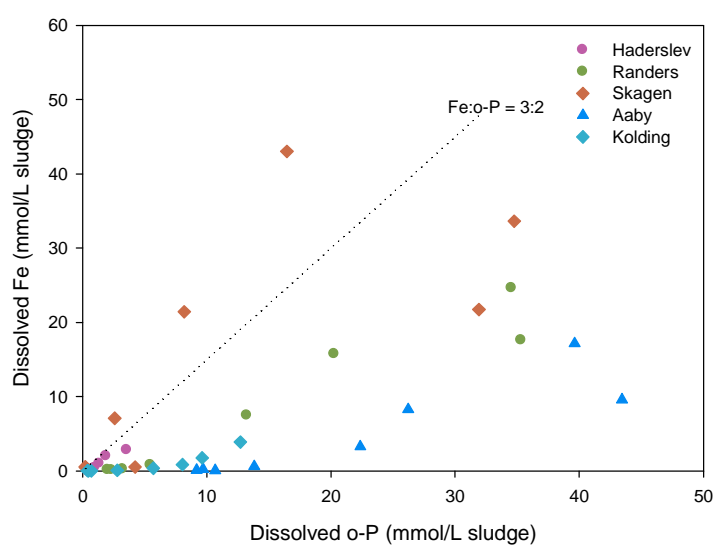


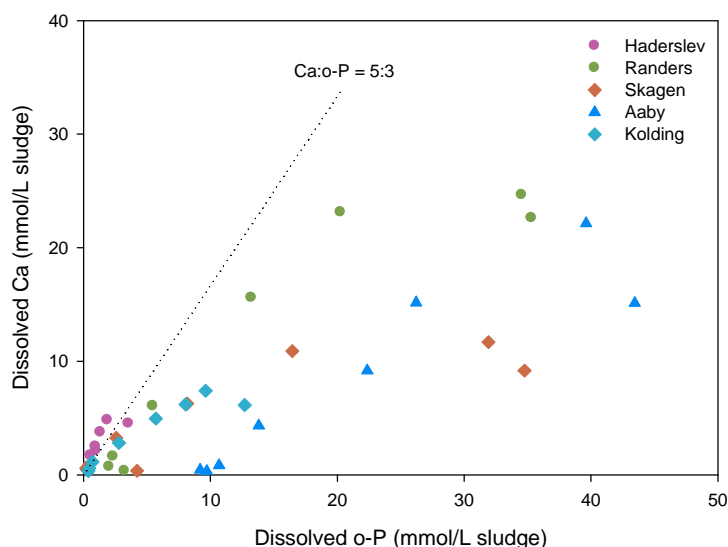
Figure 8: Metal concentration in the liquid phase with respect to the concentration in raw sludge.

In several papers, it is reported that phosphate precipitate as vivianite  $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  as the main product after addition of iron coagulant (Frossard et al., 1997; Wilfert et al., 2016) i.e. the stoichiometry for Fe:o-P is equal to 1.5. Looking at data for all plants, except Skagen WWTP, more than 10 – 20 mM phosphorus is released before any iron is dissolved, after which the ratio between Fe and o-P release is close to 1.5 (Figure 9a). Thus, the data indicates that vivianite may be one of the P-minerals dissolved during acidification, but it is not the only mineral. The data support the idea of Levlin and Hultman (Levlin and Hultman, 2007), who

report that part of the phosphorus can be dissolved without a high release of iron. Sludge also contains  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  (Yi and Lo, 2003) where the stoichiometry Ca:o-P is equal to 1.67. Plotting the release of Ca as function of o-P indicates that the first mineral released may be calcium phosphate (Figure 9b), since calcium release is higher with respect to iron in the beginning. The molar amount of released o-P is more than 9-10 times higher than the released amount of magnesium and 15 times higher than the released amount of aluminium e.g. only minor amount of phosphate is bound as aluminium or magnesium salts.



(a)



(b)

Figure 9: Stoichiometry release for (a) Fe:o-P and (b) Ca:o-P

#### Release of heavy metals during acidification

Acidification of sludge was previously used as a method to release heavy metals into the liquid phase in order to easily extract them from sludge (Mingot et al., 1995; Naoum et al., 2001; Stylianou et al., 2007). Heavy metals are often found in different fractions in sludge including soluble, exchangeable, adsorbed, bound to organics and sulfides, bound to carbonate and residual components (Tessier et al., 1979; Wang et al., 2005). There are two ways to view the heavy metal release from sludge: It can be considered negative as the released heavy metals can easily be incorporated into the phosphorus fertilizer product, or positively, as it is easier to remove the heavy metals from sludge when the heavy metals are released to the liquid phase. According to Naoum et al. (Naoum et al., 2001), the remaining heavy metals in the sludge after acid treatment are stabilized in the sludge (Naoum et al., 2001). In this study, the release of heavy metals is in general low (<30%) for all the wastewater treatment plants (Figure 10), the exceptions being Zn and Cd which show a higher release at some WWTPs.

318 The main concern regarding heavy metal dissolution in this study is related to the risk of incorporation into a  
 319 precipitated fertilizer product. Therefore, some preliminary precipitation experiments have been performed  
 320 by simply increasing pH as discussed in the following section.

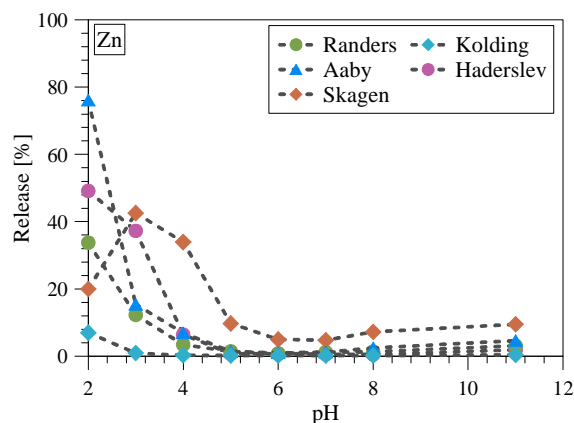
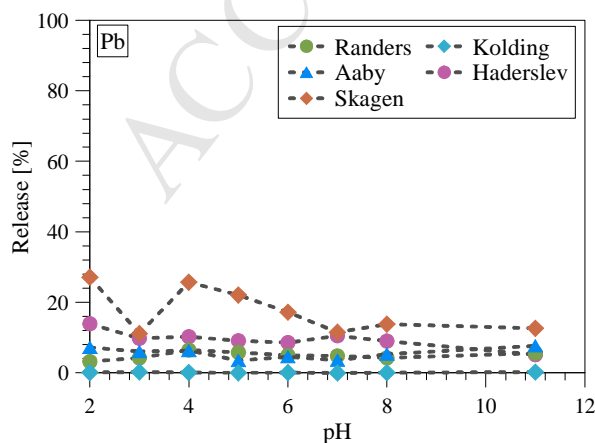
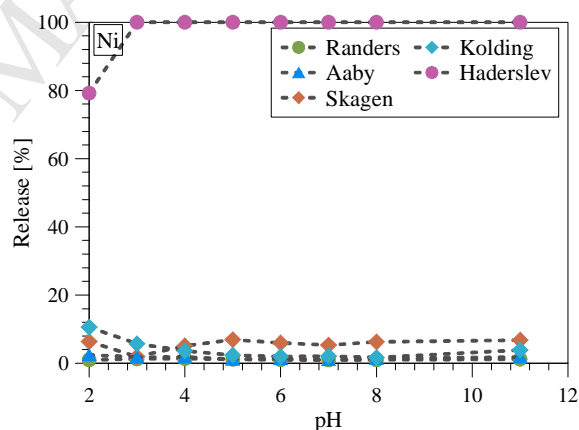
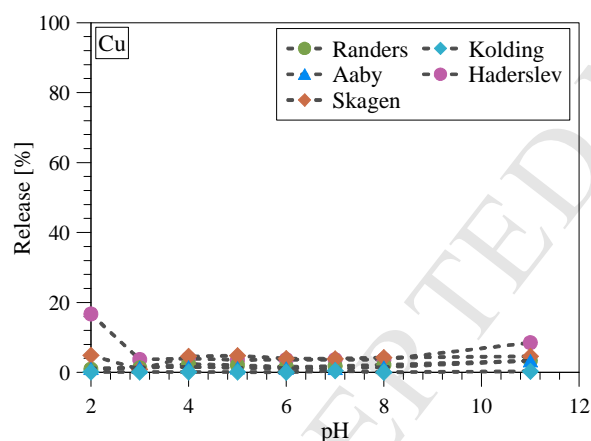
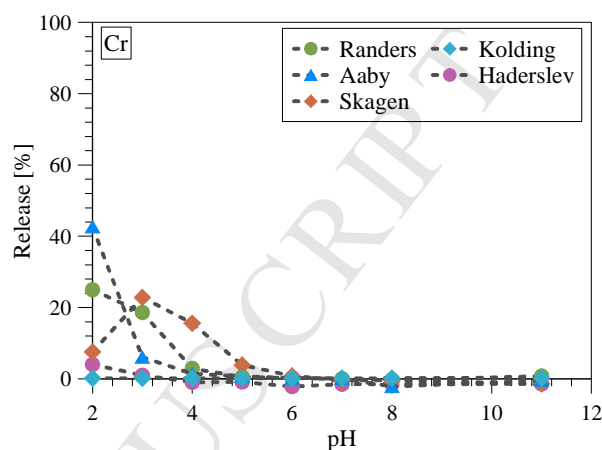
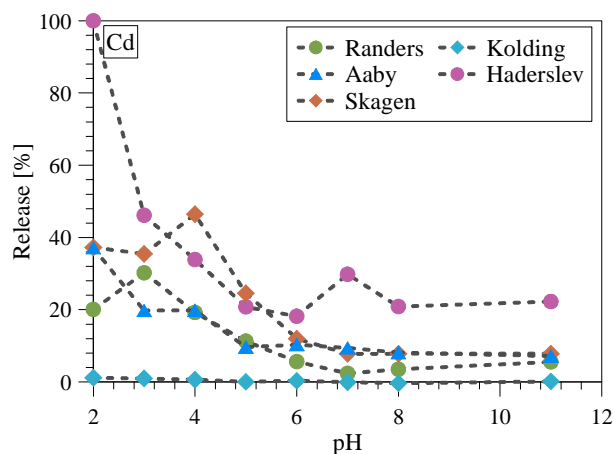


Figure 10: Release of heavy metals into the liquid phase at various pH-values, a) Cd, b) Cr, c) Cu, d) Ni, e) Pb and f) Zn.

#### Recovery of released phosphorus after acidification

The solid material was removed from acidified samples (pH 2) by centrifugation after which phosphorus was precipitated from the liquid phase by adding NaOH to pH 6, 7, 8 and 9. The phosphorus recovery increases from 53.7% at pH 6 to 80.8% at pH 9 with respect to the o-P concentration at pH 2. Besides phosphorus, the precipitate contains high amounts of calcium and iron. This indicates that phosphorus was mainly precipitated as iron phosphate and calcium phosphate (Figure 11). In the acidified sludge from Kolding WWTP more calcium was precipitated with respect to Randers WWTP. Iron precipitation was decreasing as pH was increased, and the same trend was observed for phosphorus. On the other hand, calcium precipitation increased with pH, which can be due to calcium sulfate precipitation. Calcium carbonate precipitation is unlikely, since CO<sub>2</sub> was removed during acidification. The removal of CO<sub>2</sub> might also ensure, that there are more cations in the solution that precipitate with phosphorus, since the metal-carbonate compounds originally present in the sludge is no longer an issue. Only very low amounts of Zn, Al and Mg were found in the precipitate, and thus the purity was high. The data in Figure 11 shows that precipitation follows the same trend as the dissolution of P, metals (Figure 8) and heavy metals (Figure 10) and is also in accordance with the sludge composition before acidification (Table 3), where for instance Zn has a higher concentration compared to the other heavy metals.

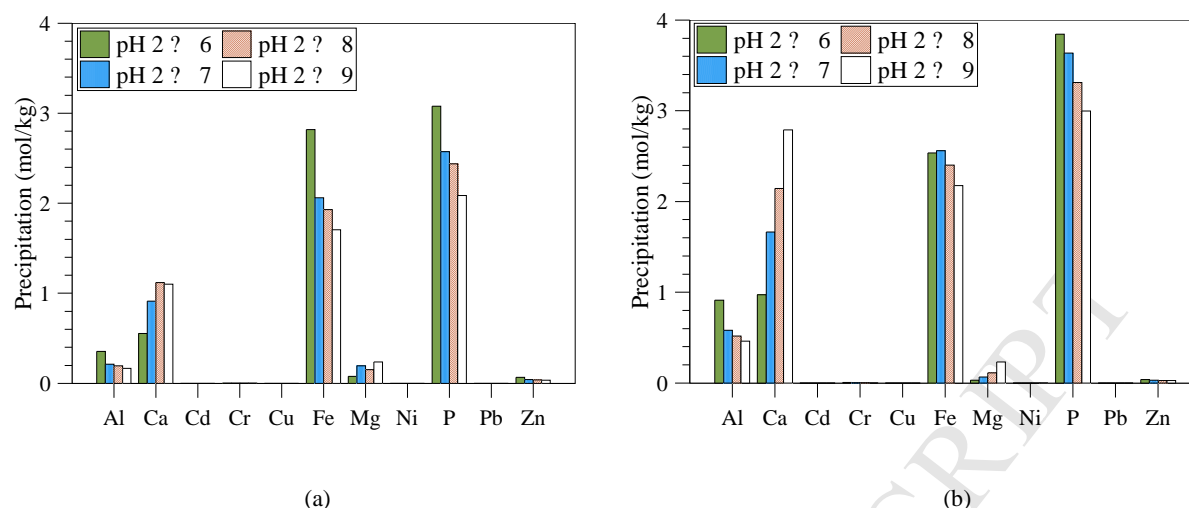


Figure 11: Precipitation at different pH (a) Randers; (b) Kolding.

### Economic evaluation of sludge acidification

Acidification of sludge improves phosphorus recovery, in particular from digested sludge. However, today it might not be cost competitive with respect to mining since the use of chemicals are rather high for acidification (0.2-0.44 mole  $\text{H}_2\text{SO}_4/\text{kg}$  sludge). Moreover, the subsequent recovery of phosphorus by either precipitation (increasing pH) or other methods also limits the economic feasibility. It is more likely that phosphorus recovery will be politically driven or that phosphorus is in high risk of depletion. In this study, the cost of acidification is around 4€/kg P based on Figure 7 and a price of  $\text{H}_2\text{SO}_4$  (95%) of 0.13€/kg. Equipment and operational costs have not been taken into account. According to (Egle et al., 2016), recovery from sludge ash is 5-6 €/kg P, recovery from digester supernatant is 6-10 €/kg P and from acidified sludge it is 9-16 €/kg P. However, the ash is used directly and separation of heavy metals is not considered, as in this study. Moreover, recovery from supernatant normally only recovers around 30-50% of the phosphorus (Pinnekamp et al., 2013), thus acidification can be a potential solution for a high phosphorus recovery process.

### Conclusion

Digested and non-digested sludge from five wastewater treatment plants were acidified by addition of  $\text{H}_2\text{SO}_4$  to dissolve phosphorus. For the five tested sludge types, 60-100 mmol o-P was released per added mol  $\text{H}_2\text{SO}_4$ . The highest phosphorus release was observed when pH was lowered to pH 2 (The sludge was exposed to acid for 1h for all the experiments). More acid was required for digested sludge as  $\text{CO}_2$  stripping increases the acid consumption. However, more phosphorus can be released from digested sludge (up to 80%) compared to non-digested sludge (25%). Simultaneously release of heavy metals was low and not a major concern. The most critical release of heavy metals were observed for Cd, Zn and Ni after acidification of non-digested sludge. High amounts of iron was released during acidification, which can be a potential problem if iron is unwanted in the phosphate product. Preliminary precipitation experiments by pH increase proved that iron is the main precipitant together with phosphorus.

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### References

- Amann, A., Zoboli, O., Krampe, J., Rechberger, H., Zessner, M., Egle, L., 2018. Environmental impacts of phosphorus recovery from municipal wastewater. *Resour. Conserv. Recycl.* 130, 127–139.  
<https://doi.org/10.1016/j.resconrec.2017.11.002>
- Antakyali, D., Meyer, C., Preyl, V., Maier, W., Steinmetz, H., 2013. Large-scale application of nutrient recovery from digested sludge as struvite. *Water Pract. Technol.* 8, 256–262.  
<https://doi.org/10.2166/wpt.2013.027>



- 386 Chipasa, K.B., 2003. Accumulation and fate of selected heavy metals in a biological wastewater treatment  
387 system. *Waste Manag.* 23, 135–143. [https://doi.org/10.1016/S0956-053X\(02\)00065-X](https://doi.org/10.1016/S0956-053X(02)00065-X)
- 388 Cordell, D., Drangert, J.-O., White, S., 2009. The story of phosphorus: Global food security and food for  
389 thought. *Glob. Environ. Chang.* 19, 292–305.
- 390 Cordell, D., Rosemarin, A., Schröder, J.J., Smit, A.L., 2011. Towards global phosphorus security: A systems  
391 framework for phosphorus recovery and reuse options. *Chemosphere* 84, 747–758.  
392 <https://doi.org/10.1016/j.chemosphere.2011.02.032>
- 393 Danish Standard, 1985a. DS 291:1985.
- 394 Danish Standard, 1985b. DS 292:1985.
- 395 Egle, L., Rechberger, H., Krampe, J., Zessner, M., 2016. Phosphorus recovery from municipal wastewater:  
396 An integrated comparative technological, environmental and economic assessment of P recovery  
397 technologies. *Sci. Total Environ.* 571, 522–542. <https://doi.org/10.1016/j.scitotenv.2016.07.019>
- 398 Frossard, E., Bauer, J.P., Lothe, F., 1997. Evidence of vivianite in FeSO<sub>4</sub>-flocculated sludge. *Water Res.* 31,  
399 2449–2454. [https://doi.org/10.1016/S0043-1354\(97\)00101-2](https://doi.org/10.1016/S0043-1354(97)00101-2)
- 400 He, Z.W., Liu, W.Z., Wang, L., Tang, C.C., Guo, Z.C., Yang, C.X., Wang, A.J., 2016. Clarification of  
401 phosphorus fractions and phosphorus release enhancement mechanism related to pH during waste  
402 activated sludge treatment. *Bioresour. Technol.* 222, 217–225.  
403 <https://doi.org/10.1016/j.biortech.2016.10.010>
- 404 Hermann, L., 2009. Rückgewinnung von Phosphor aus der Abwasserreinigung. Eine Bestandsaufnahme.  
405 Umwelt-Wissen Nr. 0929. Bundesamt für Umwelt. Bern.
- 406 Hu, P., Liu, J., Bao, H., Wu, L., Jiang, L., Zou, L., Wu, Y., Qian, G., Li, Y.Y., 2018. Enhancing phosphorus  
407 release from waste activated sludge by combining high-voltage pulsed discharge pretreatment with  
408 anaerobic fermentation. *J. Clean. Prod.* 196, 1044–1051. <https://doi.org/10.1016/j.jclepro.2018.06.153>
- 409 Klinglmair, M., Lemming, C., Jensen, L.S., Rechberger, H., Astrup, T.F., Scheutz, C., 2015. Phosphorus in  
410 Denmark: National and regional anthropogenic flows. *Resour. Conserv. Recycl.* 105, 311–324.  
411 <https://doi.org/10.1016/j.resconrec.2015.09.019>
- 412 Larsen, P., Eriksen, P.S., Lou, M.A., Thomsen, T.R., Kong, Y.H., Nielsen, J.L., Nielsen, P.H., 2006. Floc-

- 413 forming properties of polyphosphate accumulating organisms in activated sludge. *Water Sci. Technol.*  
 414 54, 257–265. <https://doi.org/10.2166/wst.2006.394>
- 415 Latif, M.A., Mehta, C.M., Batstone, D.J., 2015. Low pH anaerobic digestion of waste activated sludge for  
 416 enhanced phosphorous release. *Water Res.* 81, 288–293. <https://doi.org/10.1016/j.watres.2015.05.062>
- 417 Levlin, E., Hultman, B., 2007. Phosphorus Recovery From Sewage Sludge - Ideas for Further Studies to  
 418 Improve Leaching, in: *Integration and Optimisation of Urban Sanitation Systems: Proceedings of*  
 419 *Polish-Swedish Seminars*. pp. 61–70.
- 420 Lundin, M., Olofsson, M., Pettersson, G.J., Zetterlund, H., 2004. Environmental and economic assessment of  
 421 sewage sludge handling options. *Resour. Conserv. Recycl.* 41, 255–278.  
 422 <https://doi.org/10.1016/j.resconrec.2003.10.006>
- 423 Meulepas, R.J.W., Gonzalez-Gil, G., Teshager, F.M., Witharana, A., Saikaly, P.E., Lens, P.N.L., 2015.  
 424 Anaerobic bioleaching of metals from waste activated sludge. *Sci. Total Environ.* 514, 60–67.  
 425 <https://doi.org/10.1016/j.scitotenv.2014.12.073>
- 426 Miljøministeriet (The Danish Environmental Protection Agency), 2013. Innovationspartnerskab for  
 427 anvendelse af fosfor fra spildevand og spildevandsslam fra spildevandsforsyninger. [https://doi.org/978-](https://doi.org/978-87-92903-82-2)  
 428 [87-92903-82-2](https://doi.org/978-87-92903-82-2)
- 429 Mingot, J.I., Obrador, A., Manuel Alvarez, J., Rico, M.I., 1995. Acid extraction and sequential fractionation  
 430 of heavy metals in water treatment sludges. *Environ. Technol. (United Kingdom)* 16, 869–876.  
 431 <https://doi.org/10.1080/09593331608616325>
- 432 Müller, J. a, Günther, L., Dockhorn, T., Dichtl, N., Phan, L., Urban, I., Weichgrebe, D., 2007. Nutrient  
 433 Recycling from Sewage Sludge using the Seaborne Process. *Mov. Forward. Wastewater Biosolids*  
 434 *Sustain. Tech. Manag. Public Synerg.* 629–633.
- 435 Naoum, C., Fatta, D., Haralambous, K.J., Loizidou, M., 2001. Removal of heavy metals from sewage sludge  
 436 by acid treatment. *J. Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Environ. Eng.* 36, 873–881.  
 437 <https://doi.org/10.1081/ESE-100103767>
- 438 Pinnekamp, J., Baumann, P., Cornel, P., Everding, W., Göttlicher-Schmidle, U., Heinzmann, B., Jardin, N.,  
 439 Londong, J., Meyer, C., Mocker, M., Montag, D., Müller-Schaper, J., Petzet, S., Sonderdruck, C.S.,

2013. Stand und Perspektiven der Phosphorrückgewinnung aus Abwasser und Klärschlamm. KA –  
Korrespondenz Abwasser, Abfall, 60 10/11.
- SEG - Stadtentwässerung Göppingen, iat - Ingenieurberatung GmbH, Institut für Siedlungswasserbau, W.  
und A. (ISWA), 2014. Rückgewinnung von Phosphor aus Klärschlamm – Machbarkeitsstudie.
- Shiba, N.C., Ntuli, F., 2017. Extraction and precipitation of phosphorus from sewage sludge. *Waste Manag.*  
60, 191–200.
- Shu, L., Schneider, P., Jegatheesan, V., Johnson, J., 2006. An economic evaluation of phosphorus recovery  
as struvite from digester supernatant. *Bioresour. Technol.* 97, 2211–2216.  
<https://doi.org/10.1016/j.biortech.2005.11.005>
- Stylianou, M.A., Kollia, D., Haralambous, K.J., Inglezakis, V.J., Moustakas, K.G., Loizidou, M.D., 2007.  
Effect of acid treatment on the removal of heavy metals from sewage sludge. *Desalination* 215, 73–81.  
<https://doi.org/10.1016/j.desal.2006.11.015>
- Stössel, E., 2013. Budenheim Carbonic Acid Process – An environment friendly process for recovering  
phosphates from sewage sludge, in: International Symposium Re-Water Braunschweig, 6–7. November  
2013. Braunschweig. Germany.
- Tarayre, C., De Clercq, L., Charlier, R., Michels, E., Meers, E., Camargo-Valero, M., Delvigne, F., 2016.  
New perspectives for the design of sustainable bioprocesses for phosphorus recovery from waste.  
*Bioresour. Technol.* 206, 264–274. <https://doi.org/10.1016/j.biortech.2016.01.091>
- Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential Extraction Procedure for the Speciation of  
Particulate Trace Metals. *Anal. Chem.* 51, 844–851. <https://doi.org/10.1021/ac50043a017>
- The Danish Government, 2013. Denmark without waste 1–37. <https://doi.org/978-87-03026-59-5>
- Vaneeckhaute, C., Lebuf, V., Michels, E., Belia, E., Vanrolleghem, P.A., Tack, F.M.G., Meers, E., 2017.  
Nutrient Recovery from Digestate: Systematic Technology Review and Product Classification. *Waste  
and Biomass Valorization* 8, 21–40.
- Vardanyan, A., Kafa, N., Konstantinidis, V., Shin, S.G., Vyrides, I., 2018. Phosphorus dissolution from  
dewatered anaerobic sludge: Effect of pHs, microorganisms, and sequential extraction. *Bioresour.  
Technol.* 249, 464–472. <https://doi.org/10.1016/j.biortech.2017.09.188>

- 467 Venkiteshwaran, K., McNamara, P.J., Mayer, B.K., 2018. Meta-analysis of non-reactive phosphorus in  
468 water, wastewater, and sludge, and strategies to convert it for enhanced phosphorus removal and  
469 recovery. *Sci. Total Environ.* 644, 661–674. <https://doi.org/10.1016/j.scitotenv.2018.06.369>
- 470 Wang, J.Y., Zhang, D.S., Stabnikova, O., Tay, J.H., 2005. Evaluation of electrokinetic removal of heavy  
471 metals from sewage sludge. *J. Hazard. Mater.* 124, 139–146.  
472 <https://doi.org/10.1016/j.jhazmat.2005.04.036>
- 473 Wilfert, P., Mandalidis, A., Dugulan, A.I., Goubitz, K., Korving, L., Temmink, H., Witkamp, G.J., Van  
474 Loosdrecht, M.C.M., 2016. Vivianite as an important iron phosphate precipitate in sewage treatment  
475 plants. *Water Res.* 104, 449–460.
- 476 Wozniak, D.J., Huang, J.Y.C., 1982. Variables affecting metal removal from sludge. *Water Pollut. Control*  
477 *Fed.* 54, 1574–1580. <https://doi.org/10.2307/25041763>
- 478 Xu, Y., Hu, H., Liu, J., Luo, J., Qian, G., Wang, A., 2015. PH dependent phosphorus release from waste  
479 activated sludge: Contributions of phosphorus speciation. *Chem. Eng. J.* 267, 260–265.  
480 <https://doi.org/10.1016/j.cej.2015.01.037>
- 481 Yi, W.G., Lo, K.V., 2003. Phosphate Recovery from Greenhouse Wastewater. *J. Environ. Sci. Heal. Part B*,  
482 38, 501–509. <https://doi.org/10.1081/PFC-120021669>

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- The highest yield was obtained from digested sludge.
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- Release of heavy metals was low and not a major concern.
- Phosphate precipitates with iron at increased pH.